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Electrochemical polymerization of 1,2-ethanedithiol as a new way to synthesize polyethylenedisulfide

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Abstract

Preliminary studies of the electrochemical oxidation of 1,2-ethanedithiol in acetonitrile at platinum electrode surfaces are presented. A permanent modification of the electrode surfaces was observed after the anodic oxidation of 1,2-ethanedithiol. This modification is due to the formation of an organic polymer coating strongly tied to the electrode surfaces. This electrochemical polymerization process was studied by coupling electrochemistry and in situ electrochemical quartz crystal microbalance experiments, while ex situ X-ray photoelectron spectroscopy, Raman spectroscopy and Infrared spectroscopy were used to determine the structure of the polymer film. These spectroscopic techniques allowed us to identify the polymer films obtained by oxidation of 1,2-ethanedithiol as polyethylenedisulfide films.

Keywords: Ethanedithiol; Electrochemical oxidation; Polymer-modified electrodes

1. Introduction

For last decades, there has been a growing interest for chemically modified electrodes by electroactive conductive polymer films. Very often, these films are generated in situ by the electrochemical oxidation of aromatic compounds such as heterocyclic aromatics, in particular from the derivatives of pyrrole, thiophene, carbazole or aniline. The interest in chemically modified electrodes stems from the fact that these electrodes may impact on many different technology areas, such as electrocatalysis [1–3], electrosensors [4,5], membrane barriers [6,7], energy storage [8,9] or electrochromic display devices [10–12]. For example, for the last ten years, electropolymerization of organic monomers has been developed in our laboratory with the goal of obtaining polymer-modified electrode surfaces for specific applications such as energy storage [13], pH sensors [14–17], urea biosensors [18], copper complexation [19] or cells adhesion and proliferation [20,21]. This technique has been widely described and applied to different monomers. In particular it allowed us to find a new way to synthesize polyethyleneimine. This technique consists of initiating a polymerization reaction in the vicinity of the electrode surface and forming an insoluble polymer which precipitates onto the surface as a thin organic layer. Moreover, our research group is specialized in the electropolymerization of pure compounds or, when it is not possible to oxidize pure compounds, of very concentrated ones. For example, we have discovered an original way to electrochemically synthesize linear polyethyleneimine [22] from the anodic oxidation of pure ethylenediamine with a salt concentration of 10^{-3} M. Consequently, in this work we have tried again to synthesize polydisulfide polymer films from the oxidation of pure ethanedithiol and since it was not possible we oxidized very concentrated ethanedithiol in different solvents with a salt concentration of 10^{-3} M. Consequently, in this work, we want to show the possibility of preparing polymer films by anodic electrochemical polymerization of 1,2-ethanedithiol in acetonitrile to obtain a conductive polymer containing disulfide groups. Indeed, synthesizing such a polymer is of

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interest for the anchoring of biological molecules to metals since disulfides are known to coordinate very strongly to gold, silver, copper and platinum [23]. Moreover, disulfide polymers can also be useful for battery electrodes as was previously shown by Liu et al. [24].

2. Materials and methods

2.1. Materials

1,2-Ethanedithiol (EDT) and acetonitrile were obtained from Aldrich (analytical grade), and lithium bis(trifluoromethane)sulfonimide (LiTFSI) was from Flucka. Ethanedithiol and the lithium salt were used as received. LiTFSI was used as a supporting electrolyte at a concentration of 10^{-3} M, and was added to ethanedithiol in a glove box, from Jacomex, under a dehydrated argon atmosphere.

2.2. Apparatus and methods

The electrochemical apparatus was a classical three-electrode setup using an Autolab PGSTAT 20, from Ecochemie, potentiostat–galvanostat. Electrochemical quartz crystal microbalance (EQCM) measurements were performed using a crystal oscillating circuit PM 710 model from Maxtek. It was coupled to the potentiostat to be triggered simultaneously. The working electrode was a platinum electrode (0.785 cm^2) when cyclic voltammetry was done and a quartz crystal coated with platinum when an EQCM experiment was done. This quartz crystal was an AT-cut disk of 1.37 cm^2 surface and of 5-MHz nominal oscillation frequency. The electrode was used immediately after cleaning by nitric acid, then rinsing with water and then with ethyl alcohol, followed by drying under an argon stream. The reference electrode was a silver wire, noted as silver reference electrode (SRE), and the counter-electrode was a platinum wire. All experiments were carried out at room temperature (293 K). The solutions were purged by ultrahigh purity argon.

We used X-ray photoelectron spectroscopy to study platinum surfaces coated by oxidized EDT films. The latter ones were prepared by anodic oxidation of EDT in acetonitrile charged with LiTFSI, rinsed with ethanol and water, then dried under an argon stream. Surface sample analysis was performed using a VG Escalab 220i-XL X-ray photoelectron spectrometer using Al Kα X-ray source. Survey scans were carried out with 50-eV pass energy and a resolution of 1.0 eV. Narrow scan spectra of C_{1s} and S_{2s} regions were taken with 20-eV pass energy and a resolution of 1.0 eV. Narrow scan spectrum of $S_{2p3/2}$ region was carried out with 8-eV pass energy and a resolution of 50 meV.

We used a Fourier Transform Infrared Spectrometer Brüker IFS 66 to perform Infrared reflection absorption spectroscopy (IRRAS) spectra of the polymer-modified platinum-coated crystals. In this spectroscopic study, p and s-polarization spectra were recorded after the samples had been placed in the purged atmosphere of the spectrometer. The spectra were recorded during 1000 scans.

Raman spectra of the polymer-modified platinum surfaces were recorded with a Jobin Yvon 'LabRam' microspectrometer equipped with an internal He–Ne laser source ($\lambda = 632.8$ nm) for excitation and a liquid nitrogen-cooled charge-coupled device (CCD) detector. The power on the sample was 8 mW.

3. Results and discussion

3.1. Electropolymerization of 1,2-ethanedithiol

3.1.1. Electrochemical oxidation of EDT in acetonitrile

We used cyclic voltammetry to study the anodic oxidation of 1,2-ethanedithiol in acetonitrile. Fig. 1 shows a typical cyclic voltammogram recorded at a sweep rate of 20 mV/s for an acetonitrile solution containing 2.34 M EDT and 10^{-3} M LiTFSI. Two oxidation current peaks are present in this cyclic voltammogram at about +1.79 V and 2.16 V/SRE, but only during the first scan. These peaks correspond to the successive oxidations of the two −SH groups of EDT. Indeed, the first peak corresponds to the reaction: $HS{-}CH_2{-}CH_2{-}SH \rightarrow HS{-}CH_2{-}CH_2{-}HS^{+\circ} + e^-$, when the second peak corresponds to the reaction: $HS{-}CH_2{-}CH_2{-}SH^{\circ} \rightarrow {}^{+\circ}S{-}CH_2{-}CH_2{-}S^{+\circ} + e^-$. After the first scan, the oxidation peaks are less pronounced but the anodic current remains nearly the same from one scan to the other. These observations indicate that EDT is oxidized under anodic potentials and that the films formed at the electrode do not passivate electrode surfaces. We can also notice that it is not necessary to scan out to greater than ±3.5 V/SRE, as it was done. Indeed, the film grows if scanning is stopped after the second oxidation peak. That is why, in Fig. 2, scanning is stopped at ±3 V/SRE, that is to say just after the second oxidation peak.

3.1.2. EQCM investigation

Electrochemical Quartz Crystal Microbalance is a very useful tool in the quantitative studies of electrodeposition of molecules on electrode surfaces, that is why we have coupled an EQCM with a potentiostat to obtain coupled gravimetric curve and cyclic voltammetry. Since the EQCM was coupled to a potentiostat, we recorded the frequency changes at the platinum electrode surfaces during a cyclic voltammetry

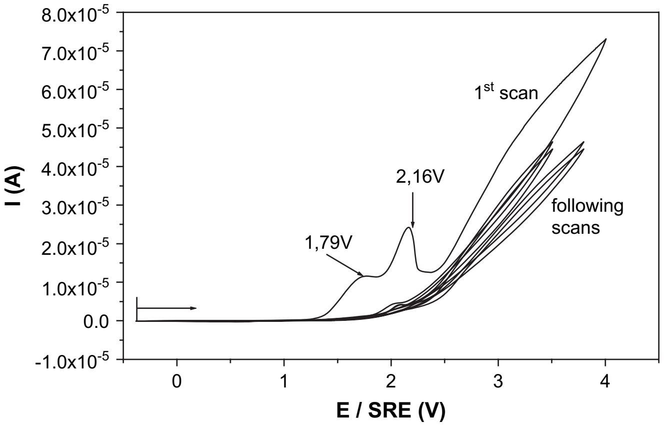

Fig. 1. Cyclic voltammogram recorded at a platinum electrode in an acetonitrile solution containing 2.34 M EDT and 10^{-3} M LiTFSI. Scan rate: 20 mV/s.

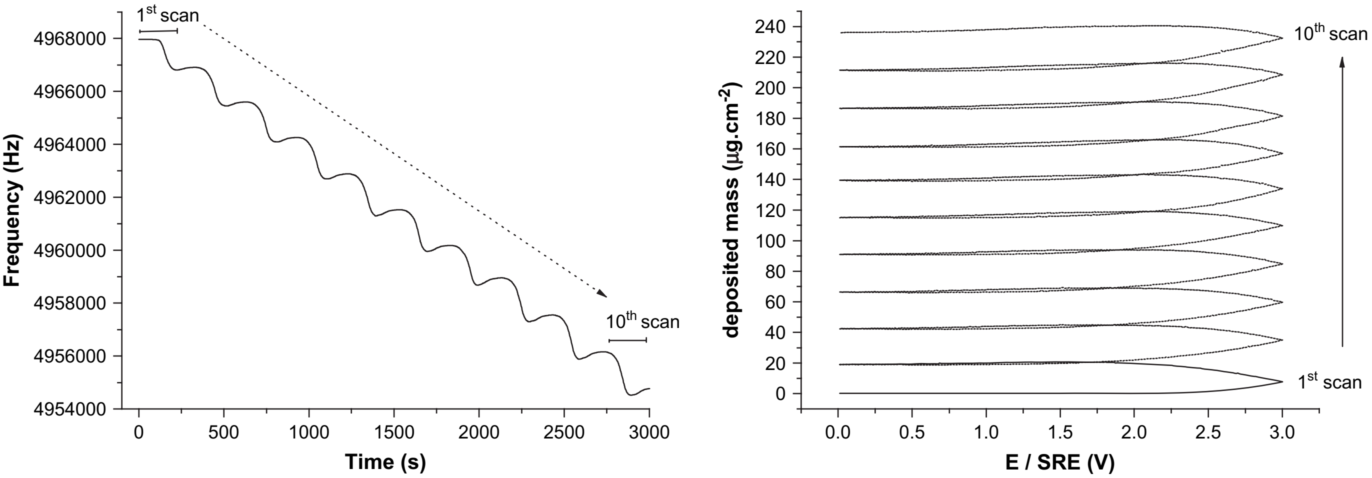

Fig. 2. Electrochemical oxidation of an acetonitrile solution containing 2.34 M EDT and 10^{-3} M LiTFSI. at a platinum electrode (10 scans were done between 0 and +3 V/SRE): (a) frequency changes as a function of time, (b) frequency changes as a function of the potential.

experiment as a function of time (Fig. 2a) and also as a function of the potential (Fig. 2b). This cyclic voltammogram experiment corresponds to the oxidation of an acetonitrile solution containing 2.34 M EDT and 10^{-3} M LiTFSI at a sweep rate of 20 mV/s and during 10 scans. We can observe in Fig. 2a that the oxidation of EDT leads to a general decrease of the platinum-coated quartz frequency. This frequency changes, Δf, can be converted into mass variations Δm (in $\mu g\,cm^{-2}$) of the active surface area of the platinum electrode (we obtained Fig. 2b). The frequency changes are converted through the Sauerbrey equation: $\Delta f = -2\Delta m n f_0/A\sqrt{\mu_q \rho_q}$ [25], where f_0 is the resonant frequency of the quartz resonator, n is the harmonic number of the oscillations (here $n = 1$), A is the piezoelectrically active surface area, ρ is the quartz crystal density ($\rho = 2.648\ g\,cm^{-3}$), and μ is the shear modulus of quartz ($\mu = 2.947 \times 10^{11}\ g\,cm^{-1}\,s^{-2}$).

Consequently, Fig. 2b gives the deposited mass on the electrode surface as a function of the potential. The weight increase begins to be observed starting from 2.0 V/SRE during the first cycle. The deposited mass continues to increase as far as the potential is superior to 2.0 V/SRE. We can also observe that the deposited mass increases for subsequent scans and that the deposited mass is about the same for each cycle. So, the film synthesized at the electrode surface grows upon repeated potential cycles. Consequently, this film is a conductive film since a non-conductive film leads to the passivation of the working electrode, so the coating cannot continue to grow upon repeated potential cycles.

3.2. Film analysis

For X-ray photoelectron, Raman and IR analysis, the films were deposited on platinum electrodes by anodic oxidation of EDT in acetonitrile charged with LiTFSI.

3.2.1. XPS chemical analysis

To control the nature of the coating, XPS chemical analysis has been performed on oxidized EDT modified platinum electrode materials. Even after thorough rinsing by pure water and ethyl alcohol, then drying under vacuum, the surface of the coating showed the presence of the supporting salt LiTFSI since we can observe one O_{1s} peak at a binding energy BE = 535.0 eV and one N_{1s} peak at BE = 403.9 eV (Fig. 3a). Moreover, this XPS spectrum indicates that oxidized EDT gave one C_{1s} peak at BE = 288.5 eV, one S_{2s} peak at BE = 231.0 eV and two $S_{2p3/2}$ peaks at BE = 165.3 eV and BE = 164.0 eV (these binding energies fit well with those already published [26,27]). Fig. 3b–d shows narrow range scans for C_{1s}, S_{2s} and $S_{2p3/2}$, respectively. Comparing these binding energies with those already published, we can deduce that C_{1s} peak is indicative of C–C or C–S bonds, that $S_{2p3/2}$ peaks at 165.3 eV and 164.0 eV correspond to S–S bond and C–S bond of R–S–S–R molecule, respectively, and that the C/S atomic ratio deduced from XPS intensities is 1 for the film formed by oxidation of EDT. Consequently, we propose that the oxidation of EDT leads to a polyethylenedisulfide whose structure is: $-(S-S-CH_2-CH_2)_n-$.

3.2.2. Raman spectroscopy

Raman spectra from oxidized EDT were performed to obtain additional information about the synthesized films on the platinum electrode surfaces. A typical spectrum of the film obtained from the oxidation of EDT in acetonitrile is shown Fig. 4 and allowed us to identify some characteristic vibration bands of polydisulfides: asymmetric and symmetric C–H stretchings at 2948 and 2904 cm^{-1}, respectively, C–H deformation at 1410 and 1280 cm^{-1}, C–C stretching at 1051 cm^{-1}, C–S out of plane vibration band at 731 cm^{-1} and S–S stretching at 505 cm^{-1}. On the contrary, no S–H vibration band was observed between 2500 and 2600 cm^{-1}. Consequently, Raman spectrum seems to confirm that the oxidation of EDT leads to the polyethylenedisulfide $-(S-S-CH_2-CH_2)_n-$.

3.2.3. Infrared spectroscopy

The IRRAS spectrum of the deposited films obtained from the oxidation of EDT in acetonitrile is shown Fig. 5 and confirms

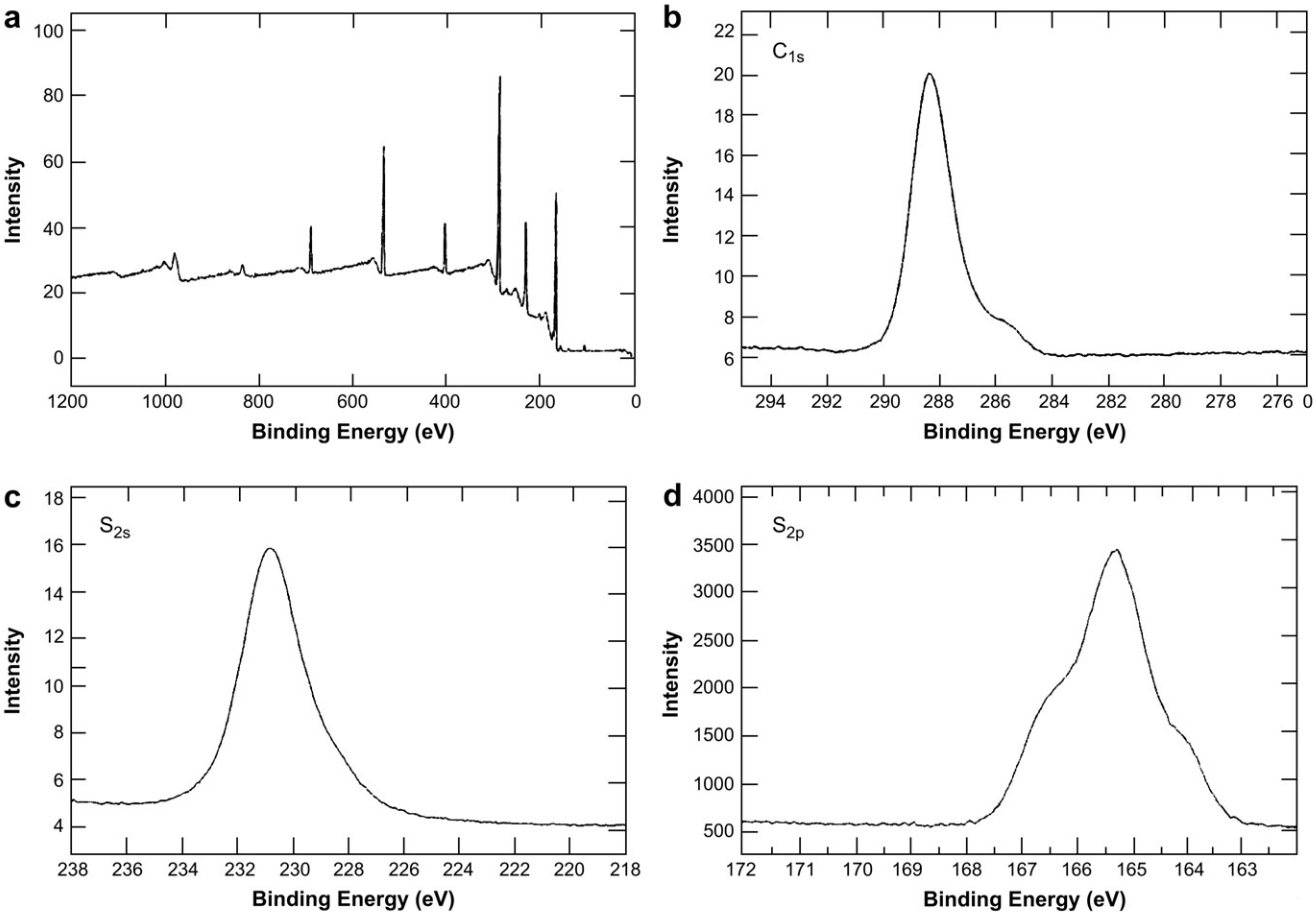

Fig. 3. (a) Survey-scan X-ray photoelectron spectroscopy of oxidized EDT modified platinum surfaces; (b) narrow scans for C_{1s}, (c) S_{2s}, (d) $S_{2p3/2}$.

Raman and XPS analyses. Indeed, the main characteristic vibration bands of the polyethylenedisulfide film appear in the IRRAS spectrum of oxidized EDT: C–H deformation at 1410 cm^{-1} and 1260 cm^{-1}, C–S vibration bands at 1200 cm^{-1} and 1100 cm^{-1} and C–S out of plane vibrations at 700 cm^{-1}. These peaks fit well with those obtained from similar compounds such as polyethylenesulfide or polypropylenesulfide [27]. We could also notice that no S–H vibration band was observed in the IRRAS spectra (if this band had appeared, it would have located between 2500 and 2600 cm^{-1}).

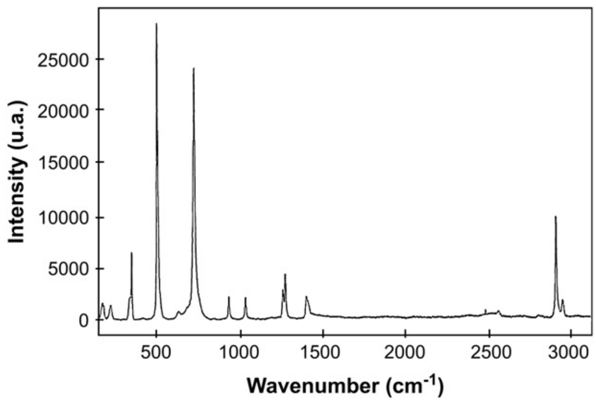

Fig. 4. Raman spectrum of oxidized EDT modified platinum surface.

3.3. Electropolymerization mechanism

Previous studies by Hammerich and Svensmark [28] on the electrochemical oxidation of thiols and related compounds on noble metal electrodes have shown that the electrochemical oxidation process of a thiol, noted R–SH, involves the initial formation of the $RS^{+\bullet}$ radical cation, followed by the formation of the $RS^{\bullet}$ radical and by the dimerization to the disulfide.

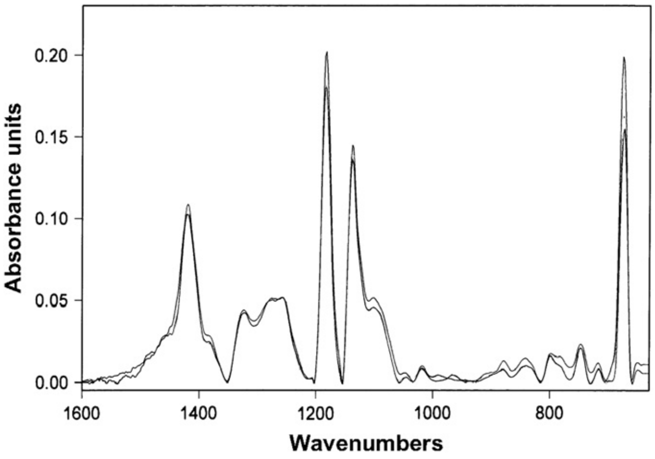

Fig. 5. IRRAS spectrum of oxidized EDT modified platinum surface.

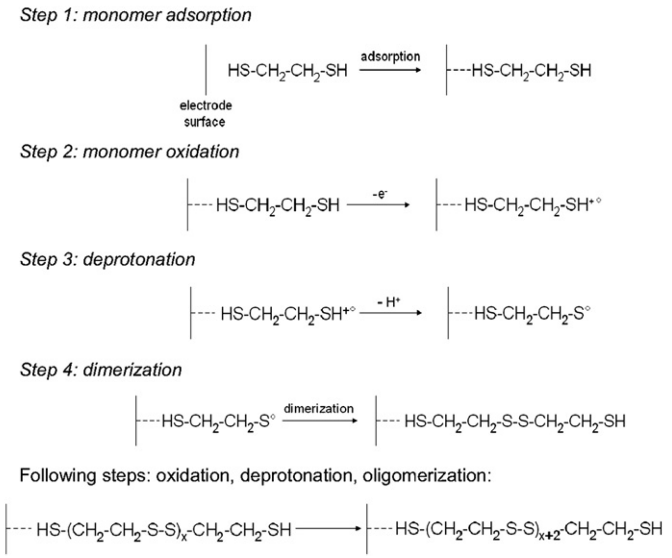

Fig. 6. Electropolymerization mechanism leading 1,2-ethanedithiol to polyethylenedisulfide.

Consequently, we took the anodic oxidation of 1,2-ethanedithiol, the mechanism described in Fig. 6. The first step is adsorption of monomer on the platinum surface electrode. Then the monomer is oxidized with the loss of an electron and the formation of a cation radical. This step corresponds to the oxidation peaks observed in Fig. 1. This step is followed by a deprotonation with formation of a radical, which dimerizes to the disulfide. Then, other sequences oxidation–deprotonation–oligomerization take place to form a polymer film. Therefore, a polyethylenedisulfide $-(CH_2-CH_2-S-S)_n-$ grows progressively on the electrode surface.

4. Conclusion

We have shown that it is possible to form polymer films by electrochemical oxidation of 1,2-ethanedithiol in acetonitrile. Electropolymerized films have been studied using X-ray photoelectron spectroscopy, Raman spectroscopy and Infrared reflection spectroscopy. It appeared that the polymer film formed on platinum electrodes was polyethylenedisulfide whose structure is $-(CH_2-CH_2-S-S)_n-$. An electropolymerization mechanism consisting of successive oxidation, deprotonation and oligomerization was also proposed. Moreover, the electrosynthesized polyethylenedisulfide films are conductive, strongly tied to the electrode surfaces and contain many sulfur atoms. These properties are promising for many different applications including electrochemical sensors, surface grafting or energy storage.

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